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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to equipment equipped with the function which cleans the inside of equipment especially about the equipment for manufacturing semiconductor memory equipment and a semiconductor device.
[0002]
[Description of the Prior Art] In recent years, high integration is demanded from the semiconductor memory equipment using capacitors, such as DRAM (Dynamic Random Access Memory) and FeRAM (Ferroelectric Random Access Memory), or the memory mixed loading LSI. A capacitor needs to decrease the area occupied on a substrate, without decreasing the electrostatic capacity C of the capacitor expressed with C=epsilon 0epsilonS/d (however, the epsilon0:dielectric constant of vacuum, the specific inductive capacity of epsilon:dielectric, S:electrode-surface product, d: dielectric thickness), in order to realize high integration. Therefore, making the configuration of a capacitor into the spacial configuration called a trench mold and a stack mold conventionally, making dielectric thickness d small, etc. are proposed.
[0003] However, while a production process becomes complicated since it is necessary with improvement in a degree of integration to make it more complicated solidification structure when integrating a capacitor highly by making it a spacial configuration, the margin of thin film formation or pattern formation also becomes narrower. For this reason, when manufacture effectiveness is taken into consideration, there is a limit in usable solidification structure. Moreover, since it becomes easy to produce current leak so that the dielectric thickness d becomes thin when integrating a capacitor highly by making dielectric thickness d thin, it is difficult to make the above thin to some extent from a viewpoint of utilization.
[0004] So, recently, new dielectric materials with high specific inductive capacity epsilon are expected for high integration of the further capacitor. Current and specific inductive capacity epsilon are examined for ferroelectrics, such as a dielectric of Ta2O5 grade, PZT [(Pb, Zr) TiO3], BST [(Ba, Sr) TiO3], STO [SrTiO3], and SBT [SrBixTayOz], etc. as high dielectric materials. In order for oxygen to escape from these dielectric materials at the time of heat treatment, even if it oxidizes, it is necessary to use the conductor which does not oxidize easily, or the existing conductive matter as an electrode material. Since it is such, Pt, Ru and Ir of a platinum group, and RuO2 grade attract attention as an electrode material. In order to manufacture a capacitor with these dielectric materials and electrode materials, it is studied that the coverage in a detailed clearance or the level difference section performs membrane formation and etching by the good CVD method and the dry etching approach using the plasma.
[0005] Generally, in a CVD system, the by-product of a membrane formation reaction adheres to equipment walls, piping walls, etc. other than on a wafer, and an etching resultant adheres to an equipment wall also with a dry etching system. These affixes will remain as unnecessary deposition film. this unnecessary deposition film -- many -- by repeating processing for several wafers, stress is

produced by the difference in a coefficient of thermal expansion with the increase of thickness, and a substrate etc., and it separates and falls, and becomes the cause of a foreign matter. Therefore, in order to raise the yield, it is necessary to remove the unnecessary deposition film. There is cleaning removed by gas or the plasma, without carrying out wet washing and atmospheric-air disconnection which carry out atmospheric-air disconnection of the equipment, and are washed with a solvent or a drug solution as the removal approach of the unnecessary deposition film. In order that wet washing may carry out atmospheric-air disconnection, the stop time of equipment becomes long, but since cleaning is not accompanied by atmospheric-air disconnection, it can remove the unnecessary deposition film in a short time farther than wet washing.

[0006] For example, supply the halogen system gas of ClF3 and NF3 grade in equipment, it is made to react with an unnecessary deposit using heat or the plasma as an approach of cleaning the unnecessary deposit of the CVD system which forms the ingredient of W, Si, and Si3N4 grade, and the cleaning approach which generates and exhausts the high halogenation compound of vapor pressure is proposed by JP,1-92385,A, JP,4-155827,A, JP,4-181734,A, JP,7-78808,A, etc.

[0007]

[Problem(s) to be Solved by the Invention] Although the combination of a high dielectric constant ingredient and the electrode of a platinum group is promising in order to form the capacitor which can be integrated highly as mentioned above, it becomes a problem how the unnecessary deposit produced in membrane formation equipment and the etching system of the above-mentioned quantity dielectric constant ingredient and an electrode is cleaned. The above-mentioned quantity dielectric constant ingredient contains alkaline earth metal, Pb, Zr, Ti, Bi, etc., and the report of the cleaning approach is not conventionally made in the unnecessary deposit containing these elements or platinum group metals.

[0008] the approach using mixed-gas systems, such as Ar/Cl2, Ar/CF4, Ar/SF6, Ar/CF4 / O2, and Ar/HBr, as the etching approach of the dielectric materials of a high dielectric constant -- the 63rd volume of application physics -- the 11th -- it is reported by No. p1139-1142. Moreover, by JP,6-151383,A, BaTiO3 is made applicable to etching and the approach of etching by the mixed-gas system of organic gas, such as a hydrocarbon and alcohol, and a halogen and rare gas is reported. As for each of these approaches, ion assistance has the need.

[0009] using the above-mentioned approach for cleaning of an equipment wall or a piping wall, since each above-mentioned etching approach needs ion assistance although applying these etching approaches as the cleaning approach is also considered -- equipment -- constitutionally -- rather -- being difficult . Moreover, as shown in drawing 8 , since vapor pressure is very low (drawing 8 : a chemistry great dictionary and chemistry handbook), the halogenide of alkaline earth metal, Pb, or platinum group metals is difficult for exhausting the halogenide of an unnecessary deposit out of equipment efficiently as a gas.

[0010] The purpose of this invention is to offer the cleaning approach for cleaning the interior of the equipment which forms or etches the ingredient containing an alkaline earth metal.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, according to this invention, the following cleaning approaches are offered. Namely, the membrane formation means for forming the film containing alkaline earth metal on a substrate, And it is the cleaning approach of semiconductor fabrication machines and equipment equipped with at least one side of the etching means for etching the film containing the alkaline earth metal on a substrate. It is the cleaning approach of the semiconductor fabrication machines and equipment containing a complex chemically-modified [which exhausts the gas which introduced the gas which makes said alkaline earth metal complex-ize in said semiconductor fabrication machines and equipment, was made to complex-ize said alkaline earth metal in the unnecessary deposit in said equipment, and was generated] degree.

[0012]

[Embodiment of the Invention] Hereafter, the gestalt of 1 operation of this invention is explained.

[0013] The unnecessary deposit adhering to the wall of the equipment which forms and etches electrode

materials, such as a dielectric containing alkaline earth metal, etc. Pb, etc., a ferroelectric, and a platinum group, contains metallic elements which are configuration elements of these film, such as alkaline earth metal, Pb, and a platinum group. In order to clean these deposits, without opening equipment to atmospheric air, it is the compound of the above-mentioned metallic element, and it is necessary to make a compound with high vapor pressure generate. Then, about Ba, Sr, Ti, Pb, Zr, and Pt, this invention persons investigated the vapor pressure of a compound, and looked for the promising compound. Consequently, as shown in drawing 8 , the organometallic complex of beta diketone system or a cyclopentadienyl ring system was understood that vapor pressure is relatively high as compared with the halogenide. Therefore, it is thought by making these organometallic complexes generate that an unnecessary deposit is removable out of equipment as matter with high vapor pressure. However, in drawing 8 , DPM is [Hexafluoroacetylacetone (C5HF 6O2) and Cp of Dipivaloylmethane (C11H19O2) and HFAC] the abbreviated names of cyclopentadienyl (C5H5). Moreover, since Ba(DPM) 2 and Sr (DPM) 2 grade are compounds used as material gas when forming BaSrTiO3 film among the organometallic complexes shown in drawing 8 , it can be surmised that these are removable out of equipment the condition at the time of membrane formation with those with a gas, and the conditions at the time of membrane formation.

[0014] Then, when artificers checked by experiment, by supplying the gas of beta diketone system or a cyclopentadienyl ring system in equipment, the organometallic complex of metallic elements, such as the alkaline earth metal and Pb in an unnecessary deposit, and a platinum group, was generated, and it was checked that cleaning can be performed.

[0015] Moreover, since the free-energy value is low and stable when the unnecessary deposit is the oxide of BaSrTiO3 grade (deltaG(BaO) =-520 KJ/mol/K, deltaG(RuO) =-560 KJ/mol/K), the generation reaction of an organometallic complex cannot progress easily thermodynamically. Then, after performing the process which returns an oxide film, it is possible by making the above-mentioned compound generate to promote cleaning. By this reduction, an oxide serves as hydrides, such as metals, such as Ba, Sr, Ti, etc. with a comparatively large free-energy value, or BaH, SrH, TiH. Then, by supplying the gas of beta diketone system or a cyclopentadienyl ring system, a complex-ized reaction becomes easy to progress and an organometallic complex can be generated.

[0016] (Gestalt 1 of operation) The membrane formation / cleaning approach using the CVD processor and this equipment of the sheet processing mold equipped with the cleaning function is first explained as a gestalt of the 1st operation.

[0017] The CVD system of the gestalt of this operation is equipment for forming TiO(Ba, Sr)3 film (the BST film being called) of a ferroelectric on a wafer 12 (drawing 1). This CVD system has the chamber 11 made from aluminum which is the reactor which performs a membrane formation reaction, the holder 113 which supports a wafer 12, and the gas shower head 14 made from aluminum which makes homogeneity supply reactant gas on a wafer, as shown in drawing 1 . The holder 113 is equipped with the heater 13 made from the ceramics for heating a wafer 12. Moreover, the feeders 15s, 16s, and 17s which gasify Ba (DPM)2, Sr (DPM)2, and TiO (DPM)2 which become a membrane formation raw material through the gas supply piping 110, respectively, and supply them are connected to the chamber 11 through Bulbs 15v, 16v, and 17v. However, DPM is the abbreviated name of Dipivaloylmethanate (C11H19O2).

[0018] Moreover, 18s of DPM feeders which supply DPM which is a kind of beta diketone as cleaning gas is connected to the gas supply piping 110 through bulb 18v. Furthermore, 19s of H2 feeders is also connected to the gas supply piping 110 through bulb 19v. Between bulb 19v and the gas supply piping 110, plasma room 20p for generating H2 plasma is arranged, and microwave generator 20w is connected to plasma room 20p.

[0019] Moreover, the exhauster 24 is connected to the chamber 11 through the piping 21, which exhausts membrane formation material gas cleaning gas. The conductance bulb 23 for controlling the pressure inside a chamber is attached in piping 21. A chamber 11, the gas supply piping 110, and piping 21 are covered at the heater 22 which heats these, in order to prevent that a resultant adsorbs.

[0020] Moreover, the mass spectroscope (QMS) 25 for observing the percentage of completion of a

cleaning reaction is connected to the chamber 11. Aging of a resultant yield can be grasped by incorporating the reaction generation gas under cleaning to a mass spectroscope 25.

[0021] The process which uses the CVD system of drawing 1 and forms the BST film on a wafer 12 next is explained.

[0022] Evacuation of the inside of a chamber 11 is carried out with an exhauster 24, a wafer 12 is laid on a holder 113 from non-illustrated load lock equipment in this condition, and a heater 13 is heated at 400 degrees C which is membrane formation temperature, and it waits until a wafer 12 reaches a thermal equilibrium state. With the equipment of drawing 1 , in order to equalize the temperature distribution of a wafer 12, size of a heater 13 was made larger than the size of a wafer 12, and the recess of heat has increased the heat input to a large wafer periphery. Moreover, the wall and piping 110 and 21 of a chamber 11 were heated at 250 degrees C at the heater 22. Although this CVD system is the so-called cold wall type which heats a wafer 12 to about 300 degrees C - 750 degrees C, and forms membranes of equipment, it also heats a chamber 11, and piping 110 and 21 grades at about 250 degrees C at a heater 22, and he is trying for material gas not to condense it to an equipment wall, since the vapor pressure of membrane formation material gas is relatively low.

[0023] Then, Bulbs 15v, 16v, and 17v were opened, Ba (DPM)2, Sr (DPM)2, and TiO(DPM)2 gas was passed, respectively, and the BST film of 30nm of thickness was formed. Displacement was controlled by the conductance bulb 23 to become a desired pressure at this time. After membrane formation, with non-illustrated load lock equipment, the wafer [finishing / membrane formation] 12 is taken out and membranes are formed by carrying another wafer 12 in a holder 113. Thus, membranes are formed to two or more wafers 12 one after another, without opening a chamber 11.

[0024] By this membrane formation, the unnecessary reaction by-product which contained Ba, Sr, Ti, etc. by the decomposition reaction of material gas arises, and these serve as an unnecessary deposit and adhere to the wall of a chamber 11 etc. Moreover, since size of a heater 13 is made larger than the size of a wafer 12 as mentioned above, the BST film is formed by the periphery of a heater 13. These unnecessary deposits turn into a foreign matter mixed in the BST film of a wafer 12 by the ability being able to become thick, while exchanging a wafer 12 one after another and repeating membrane formation repeatedly, separating and falling, or winding up by gas flow. For this reason, it becomes the cause which causes defects, such as short-circuit and an open circuit, in the capacitor formed on a wafer 12. Moreover, with degasifying from an unnecessary deposit, the partial pressure of gas in a chamber 11 changes, and the membraneous quality for every wafer 12 becomes unstable. then, the purpose which prevents these problems -- a wafer 12 -- several sheets -- equipment is cleaned whenever it processes.

[0025] Hereafter, the cleaning approach of the CVD system of drawing 1 is explained.

[0026] In the CVD system of the gestalt of this operation, when continuation membrane formation was carried out more than 1 lot (25 wafers), it turned out that it is in the inclination for the number of foreign matters mixed in the BST film to increase. Then, whenever it formed 25 wafers, cleaning by DPM was carried out in the following procedure. First, after the load lock equipment whose wafer 12 which formed membranes is not illustrated drew out, the inside of a chamber 11 was exhausted. Moreover, the heating conditions of heaters 13 and 22 made a holder 113, a chamber 11, and temperature of piping 110 and 21 the same temperature as the time of membrane formation by making it the same as the time of membrane formation.

[0027] Next, bulb 18v was opened, from 18s of DPM feeders, DPM gas was supplied and the conductance bulb 23 adjusted displacement like the time of membrane formation. Thereby, Ba, Sr, and Ti which are contained in an unnecessary deposit react with DPM, and generate the organic complexes Ba (DPM)2, Sr (DPM)2, and TiO (DPM)2 with comparatively high vapor pressure. In the gas of beta diketone systems, such as DPM, keto form and the enol form which is easy to emit a proton are reversibly intermingled like drawing 2 . It is thought that metals, such as a proton of an enol form, Ba, and Sr, permute a complex-ized reaction, and it progresses. these compounds are exhausted with an exhauster 24 -- it was alike rattlingly and the unnecessary deposit was cleaned more. This gas cleaning was carried out for 90 minutes.

[0028] When the gas in the chamber 11 at the time of cleaning was measured with the mass

spectroscope 25 and the cleaning reaction was measured, as shown in drawing 3 , Ba2+ ion was checked after supply initiation of DPM gas. From this, Ba in an unnecessary deposit was gasified by the above-mentioned reaction, and it was checked that cleaning is advancing. Moreover, after 60 minutes had passed since cleaning initiation, in spite of having continued supply of DPM gas, the ion peak intensity of Ba2+ ion was set to this level supply before of DPM gas, and it has been checked that cleaning had been completed.

[0029] Moreover, since it was thought in an unnecessary deposit that a part of Ba, Sr, and Ti [at least] exist as an oxide, artificers cleaned, after performing the reduction process beforehand, in order to speed up advance of cleaning. In this case, first, before passing DPM gas in a chamber 11, microwave was supplied to H2 plasma room 20p, H radical was generated, and this H radical was drawn in the chamber 11. H radical and the unnecessary deposit were made to react by this, and the oxide in an unnecessary deposit was returned. After that, making it the same as the time of membrane formation, the temperature of a holder 113, the temperature of a chamber 11, and the temperature of piping 110 and 21 supplied DPM gas like the above-mentioned cleaning approach, and while the conductance bulb 23 adjusted displacement, they cleaned. This gas cleaning was carried out for 30 minutes.

[0030] When the gas in the chamber 11 at the time of cleaning was similarly measured with the mass spectroscope 25, the cleaning reaction was measured and a reduction process was given as shown in drawing 3 , it has checked that the ion peak intensity of Ba2+ ion became higher than the case where a reduction process is not performed, and cleaning had ended it in about 15 minutes. Therefore, it became clear by performing a reduction process that cleaning time amount can be shortened.

[0031] If it takes into consideration that cleaning has been performed by these two cleaning approaches, respectively, DPM which is beta diketone system will react with Ba, Sr, Ti, BaH, SrH and TiH, or BaO, SrO and TiO, and it will be thought that Ba (DPM)2, Sr (DPM)2, and TiO (DPM)2 are generated.

[0032] Moreover, as the cleaning approach, after returning, the approach of carrying out DPM gas supply was adopted, it was made to clean to every membrane formation 1 lot (25 wafers / 1 lot), and transition of the number of foreign matters on a repeat deed and the wafer 12 in the meantime was measured for a series of processes of membrane formation and cleaning by 20 lots. The result is shown in drawing 4 . Drawing 4 shows that transition of the number of foreign matters is low stable. Moreover, it also turns out that the number of foreign matters becomes low relatively for every cleaning. To be able to control generating of a foreign matter by cleaning is considered by these.

[0033] Therefore, in case the capacitor which uses the BST film as a dielectric film is formed with a high degree of integration on a wafer 12, by using the membrane formation / cleaning approach of the gestalt this operation, the short-circuit and open circuit by the foreign matter can be prevented, and a capacitor with a high accumulation consistency can be formed by the high yield.

[0034] Since the cleaning by DPM of the gestalt of this operation performs in the state of the same heating as the time of membrane formation, there is [an advantage that the time amount which cleaning takes can be shortened]. Moreover, since there is no temperature change, there is also an advantage that thermal stress can protect degradation of the components of a holder 113 or chamber 11 grade. Moreover, as a result of carrying out visual observation of the surface of metal of equipment after performing 20 cleanings, the cleaning which does not generate an equipment damage is possible by not seeing corrosion etc. but using this cleaning approach.

[0035] In addition, with the gestalt of this operation, although BST was used as a membrane formation membrane type, even if it uses electrode materials, such as film containing at least one or more alkaline earth metal, film containing Pb, Zr, Bi, and at least one or more Hf(s) or a platinum group (Ru, Rh, Pd, Os, Ir, Pt), and Re, Au, the same effectiveness is acquired.

[0036] Moreover, although DPM was used as cleaning gas in this example HFAC (Hexafluoroacetylacetone), TFA (Trifluoroacetylacetone) and Acetylacetone which is R1=R2=CH3 of drawing 2 , Heptafluorodimethyloctanedionate which are R1=C (CH3)3 of drawing 2 , and R2=CF2CF2CF3, R1=CH3 of drawing 2 , and Benzoylacetone which is R2=C6H5, The same effectiveness is acquired even if it uses other beta diketone system gas and cyclopentadienyl system gas (C5H5 or C5(CH3) 5), such as Dibenzoylmethanate which is R1=R2=C6H5 of drawing 2 , as cleaning

gas.
[0037] Moreover, with the gestalt of this operation, although H2 plasma was used as a reducing agent, H2S, N2H2, hydrogen halide, a hydrocarbon, etc. may be used as a type of gas which generates H radical. Moreover, effectiveness with the same said of CO which can extract O atom is acquired from the oxide of Ba, Sr, and Ti.
[0038] Moreover, in this example, although the CVD system was used as the equipment of a heat CVD method, a CVD method cannot be limited to this and a cleaning function can be given by arranging the same cleaning gas supply system and H radical supply system also about plasma-CVD equipments, such as an parallel monotonous method, an ICP method, and an ECR method. Moreover, in case it returns in the case of plasma-CVD equipment, it is also possible to make it the configuration which returns by generating the direct plasma within a chamber. In that case, it can also be made the configuration which is not equipped with H radical supply system.
[0039] In addition, since it is the same as a CVD system, an unnecessary deposit is removable in that an unnecessary deposit adheres to the interior, even if it is equipment which forms membranes by vacuum evaporationo or the spatter, although considered as the configuration which equips with a cleaning function the equipment which forms membranes by the CVD method with the gestalt of this operation like an above-mentioned CVD system by equipping vacuum-evaporationo equipment and a sputtering system with equipments for reduction, such as a DPM feeder and H radical supply. It is also possible to make it the configuration which returns by generating the direct plasma with equipment in the case of a sputtering system.
[0040] Moreover, in this example, although the heater temperature at the time of cleaning, chamber temperature, and piping temperature are the same as the time of membrane formation, in order to raise KURININGURETO further, temperature control may be performed.
[0041] In addition, in the CVD system of drawing 1 , the thing of a configuration of storing DPM in the state of gas, and sending out can be used for a DPM feeder, and also the equipment of a configuration of sending out, after making DPM of a liquid gasify can also be used for it.
[0042] (Gestalt 2 of operation) Below, the pattern formation and the cleaning approach using the dry etching system and this equipment of the sheet processing mold equipped with the cleaning function are explained as a gestalt of the 2nd operation.
[0043] The reactor section which performs an etching reaction consists of a wafer installation electrode 53 for installing the bell jar 51 made from a quartz, the flange 52 made from SUS, and a wafer 12. The wafer installation electrode 53 is equipped with the electrostatic adsorption device and the controlling mechanism of wafer temperature.
[0044] Moreover, in order to perform plasma discharge, it has the 2.45GHz microwave oscillator 54, and a microwave waveguide 55 and a solenoid coil 56. The ECR plasma is generated by the magnetic field formed with this coil 56. The wafer installation electrode 53 serves as the electrode for impressing the bias voltage for drawing ion.
[0045] In a flange 52, 57s of HBr feeders and CH4 which supply HBr, CH4, and N2 which are etching gas through gas supply piping and a bulb, respectively 58s of feeders, 59s of N2 feeders, 60s of DPM feeders which supply DPM which is gas for cleaning, and 61s of H2 feeders which supply H2 for H radical generating are connected through Bulbs 57v, 58v, 59v, 60v, and 61s, respectively.
[0046] Moreover, the exhauster 63 for controlling the pressure of the bell jar 51 interior is connected to the flange 52 through the exhaust pipe arrangement and the conductance bulb 62.
[0047] Moreover, the mass spectroscope (QMS) 64 for observing the percentage of completion of a cleaning reaction is connected to the flange 52. A mass spectroscope 64 can grasp aging of a resultant yield by incorporating the reaction generation gas under cleaning to a mass spectroscope 64.
[0048] The process which uses the dry etching system of drawing 5 and carries out patterning of the BST film on a wafer 12 next is explained.
[0049] Evacuation of the inside of a bell jar 51 is carried out with an exhauster 63, the wafer 12 with which patterning of the resist was carried out on the BST film is laid on an electrode 53 according to a non-illustrated load lock mechanism, and temperature control of the wafer 12 is carried out to 20

degrees C. Then, Bulbs 57v, 58v, and 59v were opened, while passing HBr, CH4, and N2 gas, the field was generated with the coil 56 and the ECR plasma was generated, and it etched. At this time, displacement was controlled by the conductance bulb 62 to become a desired pressure. After etching, the non-illustrated load lock mechanism drew out the wafer 12, and the inside of a bell jar was exhausted. And another wafer 12 was carried on the electrode 53, and it etched similarly. Thus, it etches to two or more wafers 12 one after another, without opening a bell jar 51.

[0050] Thus, if repeat etching is performed, a by-product occurs by the reaction of the etched film or the resist film, and etching gas, and it will adhere to bell jar 51 wall etc., and will serve as an unnecessary deposit. These separate and fall or serve as a foreign matter by gas flow which can wind up and adheres to the pattern on a wafer 12. Therefore, it becomes the cause which causes defects, such as short-circuit and an open circuit, in the capacitor formed on a wafer 12. Moreover, with degasifying from an unnecessary deposit, the partial pressure of gas in a bell jar 51 changes, and the etching reaction for every wafer becomes unstable. Then, equipment is cleaned for every processing of several wafers in order to prevent these problems.

[0051] Hereafter, the cleaning approach of the etching system of drawing 5 is explained.

[0052] In the etching system of the gestalt of this operation, since it turned out that it is in the inclination for the number of foreign matters on the BST film to increase when continuation membrane formation was carried out more than 2 lots (50 wafers), whenever it etched 50 wafers, cleaning by DPM was carried out in the same procedure as the gestalt of the 1st operation. First, after the load lock equipment whose etched wafer 12 is not illustrated drew out, the inside of a bell jar 51 was exhausted. Temperature of the wafer installation electrode 53 was made the same as the time of etching. Bulb 60v was opened, from 60s of DPM feeders, DPM gas was supplied and the conductance bulb 62 adjusted displacement like the time of etching. This gas cleaning was carried out for 90 minutes.

[0053] When the gas in the bell jar 51 at the time of cleaning was measured with the mass spectroscope 64 and the cleaning reaction was measured, as shown in drawing 6 , after starting supply of DPM gas, Ba2+ ion was checked, and it was checked that cleaning is advancing. Moreover, it has been checked that cleaning had been completed after 60-minute progress from cleaning initiation.

[0054] Moreover, like the gestalt of the 1st operation, since advance of cleaning is sped up, it can also be made the cleaning approach which cleans after performing a reduction process beforehand. In this case, before supplying DPM gas, H radical was generated in the bell jar 51 by opening bulb 61v, generating a field for H2 gas from a sink and a coil 56, and generating the ECR plasma. Thereby, the unnecessary deposition film was made to react with H radical, and the unnecessary deposition film was returned. DPM gas was supplied after that, making temperature of the wafer installation electrode 53 the same as the time of etching, and while the conductance bulb 62 adjusted displacement, it cleaned. This gas cleaning was carried out for 30 minutes.

[0055] When the gas in the chamber 11 at the time of cleaning was similarly measured with the mass spectroscope 25, the cleaning reaction was measured and a reduction process was given as shown in drawing 3 , it has checked that the ion peak intensity of Ba2+ ion became higher than the case where a reduction process is not performed, and cleaning had ended it in about 15 minutes. Therefore, it became clear by performing a reduction process that cleaning time amount can be shortened.

[0056] Moreover, as the cleaning approach, after returning, the approach of carrying out DPM gas supply was adopted, it was made to clean to every etching 2 lot (25 wafers / 1 lot), and transition of the number of foreign matters on a repeat deed and the wafer 12 in the meantime was measured for a series of processes of etching cleaning by 40 lots. The result is shown in drawing 7 . Drawing 7 shows that transition of the number of foreign matters is low stable. To be able to control generating of a foreign matter by cleaning is considered by these.

[0057] Therefore, in case the capacitor which uses the BST film as a dielectric film is formed with a high degree of integration on a wafer 12, by using the etching cleaning approach of the gestalt this operation, the short-circuit and open circuit by the foreign matter can be prevented, and a capacitor with a high accumulation consistency can be formed by the high yield.

[0058] Since the cleaning by DPM of the gestalt of this operation performs in the state of the same

heating as the time of etching, there is [an advantage that the time amount which cleaning takes can be shortened]. Moreover, since there is no temperature change, there is also an advantage that thermal stress can protect degradation of the wafer earth electrode 53 and the components of bell jar 51 grade. Moreover, as a result of carrying out visual observation of the surface of metal of equipment after performing 20 cleanings, the cleaning which does not generate an equipment damage is possible by having not seen corrosion etc.

[0059] In addition, with the gestalt of this operation, although the BST film was used as a candidate for etching, even if it uses electrode materials, such as film containing at least one or more alkaline earth metal, film containing Pb, Zr, Bi, and at least one or more Hf(s) or a platinum group (Ru, Rh, Pd, Os, Ir, Pt), and Re, Au, the same effectiveness is acquired.

[0060] Moreover, beta diketone system gas stated not only with DPM but with the gestalt of the 1st operation as cleaning gas and the gas of a cyclopentadienyl system can be used. Moreover, a reducing agent may also use H2S, N2H2, hydrogen halide, a hydrocarbon, etc. Moreover, effectiveness with the same said of CO which can extract O atom is acquired from the oxide of Ba, Sr, and Ti.

[0061] (Gestalt 3 of operation) Below, the manufacture approach of a semiconductor device is explained as a gestalt of the 3rd operation. This semiconductor device is DRAM which carried the memory cell of stacked capacitor structure in the upper part of MOSFET for memory cell selection like drawing 2 . A memory cell consists of RuO(s)2 whose lower electrode layers 92 and up electrode layers 94 of a capacitor are conductive metallic oxide, and the dielectric film 93 is constituted by TiO(Ba, Sr) 3 (Following BST is called) of a ferroelectric ingredient.

[0062] The configuration of the semiconductor device of the gestalt of this operation is explained using drawing 9 . A well 2 is formed in the top face of p mold single crystal silicon substrate 1 p molds, and the component formation field 91 is established in it by dividing a part of well 2 p mold by p mold channel stopper layer 5. The source and the drain field 8 of a n-type semiconductor are formed in the component formation field 91. The gate electrode 6 with which the perimeter was moreover surrounded by the silicon oxide layer 3 is arranged. These constitute MOSFET. In addition, the gate electrode serves as the word line of a memory cell.

[0063] The lower electrode layer 92 of a memory cell is arranged so that it may touch on this MOSFET at either the source or the drain field 8. On the lower electrode layer 92, the laminating of a dielectric film 93 and the up electrode layer 94 is carried out. These constitute the memory cell of stacked capacitor structure.

[0064] On the up electrode layer 94, the laminating of the oxidation silicone film 95, the BPSG (Boron-doped Phospho Silicate Glass) film 96, and the bit line 97 is carried out. The bit line 97 touches either the source or the drain field 8 through the conductor 98.

[0065] Below, the manufacture approach of the semiconductor device of drawing 9 is explained. first, p mold single crystal silicon substrate 1 -- an ion implantation and LOCOS -- law, a CVD method, a spatter, the etching method, etc. -- p mold -- a well, p mold channel stopper layer 5, the source and the drain field 8, the silicon oxide layer 3, and the gate electrode 6 are formed. the dry etching after forming RuO2 film which uses a magnetron RF sputtering system and turns into the lower electrode layer 92 next -- RuO2 film -- patterning -- carrying out -- the lower electrode layer 92 -- having formed .

[0066] The BST film is formed by the membrane formation approach explained with the gestalt of the 1st operation using the CVD system of drawing 1 of the gestalt of the 1st operation on this lower electrode layer 92. Patterning of the BST film is carried out by the etching approach which explained this BST film with the gestalt of the 2nd operation using the etching system of drawing 5 of the gestalt of the 2nd operation, and a dielectric film 93 is formed. Besides, patterning of the RuO2 film is formed and carried out like the lower electrode layer 92, and the up electrode layer 92 is formed.

[0067] then, the oxidation silicone film 95 -- the BPSG film 96 -- membrane formation and patterning -- carrying out -- a conductor -- the section 97 was embedded by W film and the bit line 97 was formed by forming and carrying out patterning of the W film further.

[0068] In addition, in the manufacture approach of this semiconductor device, when forming and etching the dielectric film 93 which consists of BST, it cleaned periodically by the approach which explained the

CVD system and the etching system with the gestalt of the 1st and the 2nd operation by DPM gas, and the unnecessary deposit was removed.

[0069] Thus, by the manufacture approach of the semiconductor device of the gestalt this operation, since cleaning of membrane formation equipment and an etching system was performed, the number of foreign matters mixed in a dielectric film 93 can be decreased sharply. Thereby, by the manufacture approach of the semiconductor device of the gestalt this operation, short-circuit and an open circuit of the capacitor of the semiconductor device of drawing 9 were able to be prevented, and the high yield was able to be realized.

[0070] Moreover, since the unnecessary deposit containing Ru accumulates also about the sputtering system and dry etching system which form the lower part and the up electrode layers 92 and 94 of RuO2, the unnecessary deposit containing Ru can be cleaned by attaching the supply system which supplies beta diketone system gas and cyclopentadienyl system gas, and the equipment for reduction as well as the equipment of the gestalt of the 1st and the 2nd operation. Since the number of foreign matters mixed also about the lower part and the up electrode layers 92 and 94 can be reduced by this, short-circuit and an open circuit of a capacitor can be prevented still more effectively, and the further high yield can be realized.

[0071] In addition, although the BST film was used as a dielectric film 93 and RuO2 film was used as the lower part and up electrode layers 92 and 94 with the gestalt of the 3rd operation Not only as these ingredients but as a dielectric film 93, ferroelectrics, such as a dielectric of Ta2O5 grade, PZT [(Pb, Zr) TiO3], BST [(Ba, Sr) TiO3], STO [SrTiO3], and SBT [SrBixTayOz], etc. can be used. Moreover, Pt, Ru, and Ir of a platinum group can be used as an ingredient of electrode layers 92 and 94. Also when using these ingredients, those membrane formation and etching systems can be cleaned as mentioned above. Thereby, the manufacture effectiveness of a semiconductor device can be raised.

[0072] Moreover, since these cleaning approaches do not need to open equipment, its operating ratio of equipment can improve and they can acquire the big effectiveness of the improvement in manufacture effectiveness for a semiconductor device especially at the time of mass production.

[0073] Moreover, although the gestalt of the 3rd operation described how to manufacture the semiconductor device containing a capacitor Also about the manufacture approaches, such as a semiconductor device using not only a semiconductor device but high dielectric constant ingredients, such as BST, as insulator layers, such as gate dielectric film, and a circuit apparatus using a platinum group as an electrode In that an unnecessary deposit accumulates, since it is the same, it can clean as a part of production process like the gestalt of the 3rd operation of a ****.

[0074]

[Effect of the Invention] As mentioned above, according to this invention, the cleaning approach for cleaning the interior of the equipment which forms or etches the ingredient containing an alkaline earth metal can be offered.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] In recent years, high integration is demanded from the semiconductor memory equipment using capacitors, such as DRAM (Dynamic Random Access Memory) and FeRAM (Ferroelectric Random Access Memory), or the memory mixed loading LSI. A capacitor needs to decrease the area occupied on a substrate, without decreasing the electrostatic capacity C of the capacitor expressed with C=epsilon 0epsilonS/d (however, the epsilon0:dielectric constant of vacuum, the specific inductive capacity of epsilon:dielectric, S:electrode-surface product, d: dielectric thickness), in order to realize high integration. Therefore, making the configuration of a capacitor into the spacial configuration called a trench mold and a stack mold conventionally, making dielectric thickness d small, etc. are proposed.
[0003] However, while a production process becomes complicated since it is necessary with improvement in a degree of integration to make it more complicated solidification structure when integrating a capacitor highly by making it a spacial configuration, the margin of thin film formation or pattern formation also becomes narrower. For this reason, when manufacture effectiveness is taken into consideration, there is a limit in usable solidification structure. Moreover, since it becomes easy to produce current leak so that the dielectric thickness d becomes thin when integrating a capacitor highly by making dielectric thickness d thin, it is difficult to make the above thin to some extent from a viewpoint of utilization.
[0004] So, recently, new dielectric materials with high specific inductive capacity epsilon are expected for high integration of the further capacitor. Current and specific inductive capacity epsilon are examined for ferroelectrics, such as a dielectric of Ta2O5 grade, PZT [(Pb, Zr) TiO3], BST [(Ba, Sr) TiO3], STO [SrTiO3], and SBT [SrBixTayOz], etc. as high dielectric materials. In order for oxygen to escape from these dielectric materials at the time of heat treatment, even if it oxidizes, it is necessary to use the conductor which does not oxidize easily, or the existing conductive matter as an electrode material. Since it is such, Pt, Ru and Ir of a platinum group, and RuO2 grade attract attention as an electrode material. In order to manufacture a capacitor with these dielectric materials and electrode materials, it is studied that the coverage in a detailed clearance or the level difference section performs membrane formation and etching by the good CVD method and the dry etching approach using the plasma.
[0005] Generally, in a CVD system, the by-product of a membrane formation reaction adheres to equipment walls, piping walls, etc. other than on a wafer, and an etching resultant adheres to an equipment wall also with a dry etching system. These affixes will remain as unnecessary deposition film. this unnecessary deposition film -- many -- by repeating processing for several wafers, stress is produced by the difference in a coefficient of thermal expansion with the increase of thickness, and a substrate etc., and it separates and falls, and becomes the cause of a foreign matter. Therefore, in order to raise the yield, it is necessary to remove the unnecessary deposition film. There is cleaning removed by gas or the plasma, without carrying out wet washing and atmospheric-air disconnection which carry out atmospheric-air disconnection of the equipment, and are washed with a solvent or a drug solution as the removal approach of the unnecessary deposition film. In order that wet washing may carry out

atmospheric-air disconnection, the stop time of equipment becomes long, but since cleaning is not accompanied by atmospheric-air disconnection, it can remove the unnecessary deposition film in a short time farther than wet washing.

[0006] For example, supply the halogen system gas of ClF3 and NF3 grade in equipment, it is made to react with an unnecessary deposit using heat or the plasma as an approach of cleaning the unnecessary deposit of the CVD system which forms the ingredient of W, Si, and Si3N4 grade, and the cleaning approach which generates and exhausts the high halogenation compound of vapor pressure is proposed by JP,1-92385,A, JP,4-155827,A, JP,4-181734,A, JP,7-78808,A, etc.

[Translation done.]

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CLAIMS

[Claim(s)]
[Claim 1] the membrane formation means for forming the film containing alkaline earth metal on a substrate -- and It is the cleaning approach of semiconductor fabrication machines and equipment equipped with at least one side of the etching means for etching the film containing the alkaline earth metal on a substrate. The cleaning approach of the semiconductor fabrication machines and equipment characterized by including a complex chemically-modified [which exhausts the gas which introduced the gas which makes said alkaline earth metal complex-ize in said semiconductor fabrication machines and equipment, was made to complex-ize said alkaline earth metal in the unnecessary deposit in said equipment, and was generated] degree.
[Claim 2] On a substrate, Ru, Rh, Pd, Os, Ir, Pt, Re, Au, Pb, The membrane formation means for forming the film containing at least one element in Zr, Ti, Hf, and Bi, And it is the cleaning approach of semiconductor fabrication machines and equipment equipped with at least one side of the etching means for etching said film on said substrate. The cleaning approach of the semiconductor fabrication machines and equipment characterized by including a complex chemically-modified [which exhausts the gas which introduced the gas which makes said element complex-ize in said semiconductor fabrication machines and equipment, was made to complex-ize said element in the unnecessary deposit in said equipment, and was generated] degree.
[Claim 3] It is the cleaning approach of the semiconductor fabrication machines and equipment characterized by including the process to which said cleaning process returns said unnecessary deposit before a complex chemically-modified [said] degree in the manufacture approach of a semiconductor device according to claim 1 or 2.
[Claim 4] The cleaning approach of the semiconductor fabrication machines and equipment characterized by using the thing containing either [at least] beta diketone system gas or cyclopentadienyl system gas as said gas in the manufacture approach of a semiconductor device according to claim 1, 2, or 3.
[Claim 5] A vacuum housing, the substrate attaching part arranged in said vacuum housing, and a processing means to process the substrate which said substrate attaching part holds, It has a cleaning means for removing the unnecessary deposit deposited in said vacuum housing. Said processing means The membrane formation means for forming the film containing alkaline earth metal on the substrate which said substrate attaching part holds, It has at least one side of the etching means for etching the film containing the alkaline earth metal on the substrate which said substrate attaching part holds. And said cleaning means The manufacturing installation of the semiconductor device characterized by having a means to introduce the gas which makes said alkaline earth metal contained in said unnecessary deposit complex-ize in said vacuum housing.
[Claim 6] A vacuum housing, the substrate attaching part arranged in said vacuum housing, and a processing means to process the substrate which said substrate attaching part holds, It has a cleaning means for removing the unnecessary deposit deposited in said vacuum housing. Said processing means On the substrate which said substrate attaching part holds, Ru, Rh, Pd, Os, Ir, The membrane formation

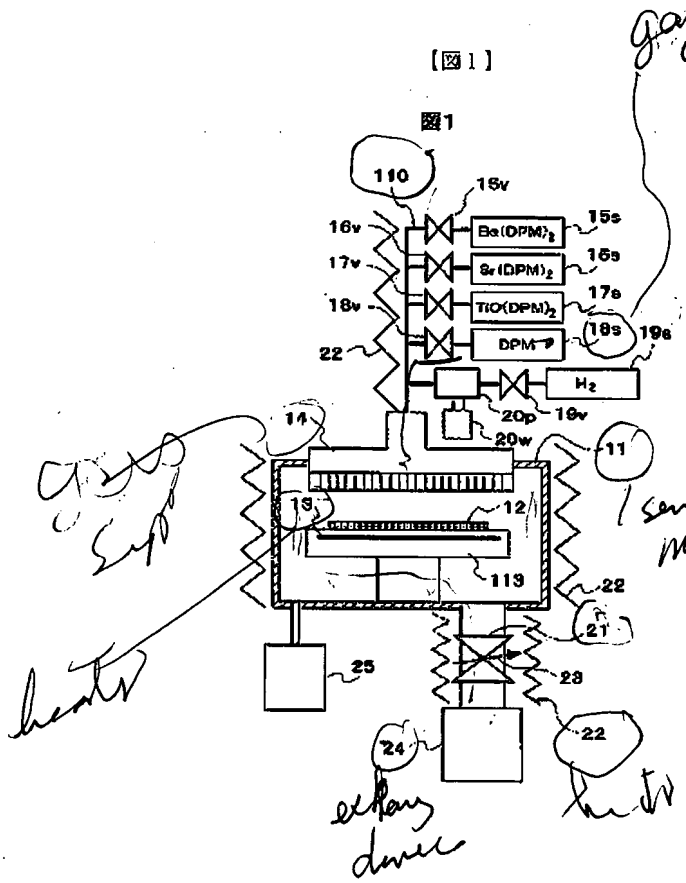
means for forming the film containing at least one element in Pt, Re, Au, Pb, Zr, Ti, Hf, and Bi, It has at least one side of the etching means for etching said film on the substrate which said substrate attaching part holds. And said cleaning means The manufacturing installation of the semiconductor device characterized by having a means to introduce the gas which makes said element contained in said unnecessary deposit complex-ize in said vacuum housing.
[Claim 7] It is the manufacturing installation of the semiconductor device characterized by having a reduction means for said cleaning means returning said unnecessary deposit in the manufacturing installation of a semiconductor device according to claim 5 or 6.
[Claim 8] It is the manufacturing installation of the semiconductor device characterized by said gas containing either [at least] beta diketone system gas or cyclopentadienyl system gas in the manufacturing installation of a semiconductor device according to claim 5, 6, or 7.
[Claim 9] It is the manufacture approach of the semiconductor device equipped with the film containing alkaline earth metal on a substrate. The process which etches said film into a desired pattern using the process or etching system which forms the film which contains said alkaline earth metal on said substrate using membrane formation equipment, It is the manufacture approach of the semiconductor device which has the process which cleans the unnecessary deposit in said membrane formation equipment or the equipment of an etching system, and is characterized by said cleaning process including the process removed by making the alkaline earth metal in said unnecessary deposit complex-ize.
[Claim 10] On a substrate, Ru, Rh, Pd, Os, Ir, Pt, Re, Au, Pb, It is the manufacture approach of a semiconductor device equipped with the film containing at least one element in Zr, Ti, Hf, and Bi. The process which etches said film into a desired pattern using the process or etching system which forms said film on a substrate using membrane formation equipment, It is the manufacture approach of the semiconductor device which has the process which cleans the unnecessary deposit in said membrane formation equipment or the equipment of an etching system, and is characterized by said cleaning process including the process removed by making said element in said unnecessary deposit complex-ize.

[Claim 11] It is the manufacture approach of the semiconductor device characterized by including a complex chemically-modified [which exhausts as a gas the product which said cleaning process introduced the gas for said complex-izing in the manufacture approach of a semiconductor device according to claim 9 or 10, and was produced by said complex-ization] degree.
[Claim 12] It is the manufacture approach of the semiconductor device characterized by including the process to which said cleaning process returns said unnecessary deposit before a complex chemically-modified [said] degree in the manufacture approach of a semiconductor device according to claim 9, 10, or 11.
[Claim 13] The manufacture approach of the semiconductor device characterized by using the thing containing either [at least] beta diketone system gas or cyclopentadienyl system gas as said gas in the manufacture approach of a semiconductor device according to claim 11.
[Claim 14] The film which contains said alkaline earth metal in the manufacture approach of a semiconductor device according to claim 9 is the manufacture approach of the semiconductor device characterized by being the dielectric film of the capacitor of said semiconductor device.
[Claim 15] The cleaning ingredient which is a cleaning ingredient for cleaning the unnecessary deposit inside the manufacturing installation of a semiconductor device, and is characterized by including either [at least] beta diketone system gas or the cyclopentadienyl system gas.
[Claim 16] The cleaning ingredient characterized by being a cleaning ingredient for cleaning the unnecessary deposit inside the manufacturing installation of a semiconductor device, and being the ingredient made to generate either [at least] beta diketone system gas or the cyclopentadienyl system gas.

[Translation done.]

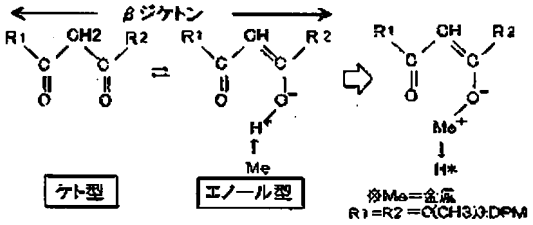
【図1】

図1



【図2】

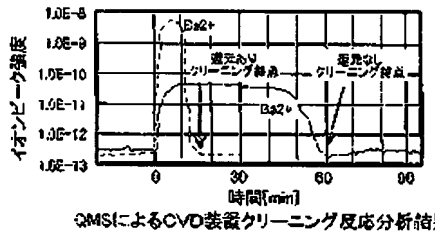
図2



βジケトンと金属との反応

【図3】

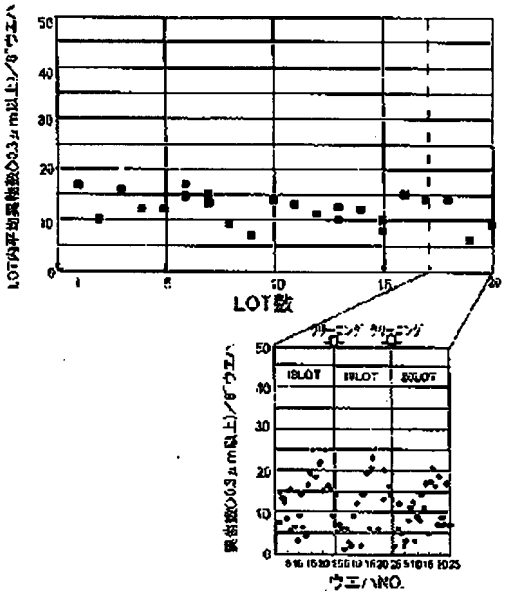
図3



QMSによるCVD装置クリーニング反応分析結果

【図4】

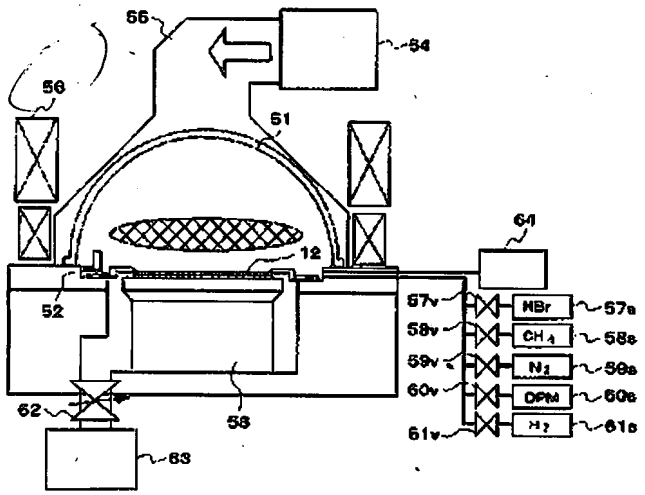
図4



CVD装置の異物数推移

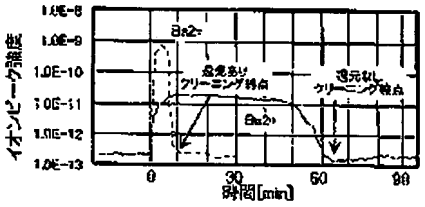
【図5】

図5



【図6】

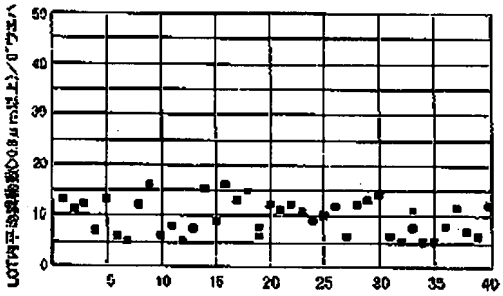
図6



QMSによるエッチング装置クリーニング反応分析結果

【図7】

図7



エッチング装置の異物数推移

【図８】

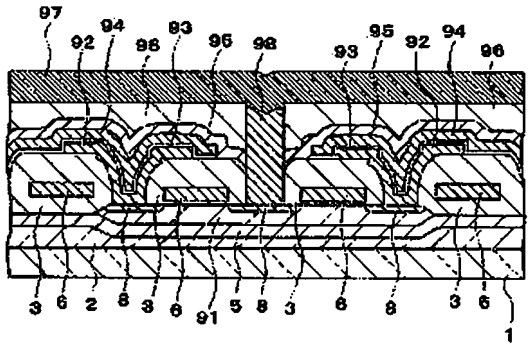
図8 アルカリ土類金属等の融点と蒸気圧

元素	化合物	融点(℃)	蒸気圧(℃/Torr)
Ba	BaF2	1355	2,272℃/760Torr
	BaCl2	963	2,089℃/760Torr
	BaBr2	847	8,031℃/760Torr
	Ba(DPM)2	219～217	238℃/0.1Torr
	Ba(Cp)2		420℃/760Torr
Sr	SrF2	1473	2,489℃/760Torr
	SrCl2	875	1,250℃/760Torr
	SrBr2	643	2,149℃/760Torr
	Sr(DPM)2		231℃/0.1Torr
	Sr(HFAC)2		220℃/0.02Torr
	Sr(Cp)2		360℃/760Torr
Ti	TiF4	1200	1400℃/760Torr
	TiCl4	-29	136℃/760Torr
	TiBr4	39	230℃/760Torr
	TiO(DPM)2		125℃/0.1Torr
Pb	PbF2	830	1,300℃/760Torr
	PbCl2	501	950℃/760Torr
	PbBr2	371	916℃/760Torr
	Pb(DPM)2	191	58～64℃/5Torr
Zr	ZrF2	932	605(s)℃/760Torr
	ZrCl2	437	331(s)℃/760Torr
	ZrBr2	450	359(s)℃/760Torr
	Zr(DPM)4	182	140～152℃/1Torr
Pt	PtF6	53(d)	
	PtCl2	370(d)	650℃/760Torr
	PtBr2	100(d)	
	Pt(HFAC)2	143～145	85℃/0.1Torr
	Pt(C5H5)(C5H5)	63～64	25℃/0.01Torr
Si 参考	SiF4	-90	-65℃/760Torr
	SiCl4	-70	58℃/760Torr
	SiBr4	5	154℃/760Torr

(s)は昇華、(d)は分解することを意味する。
DPM=(C11H19O2)
HFAC=(C5HF6O2)
Cp=C5H5

【図９】

図9



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Ｆターム(参考)　4H003 BA20 DA15 DB01 DC01 EB02
EB03 ED03 ED30
5F004 AA15 BA14 CB04 DA00 DA25
DB08 DB13
5F045 AB31 AC07 DP03 EB06 EH13

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-176807

(43)Date of publication of application : 29.06.2001

(51)Int.Cl. H01L 21/205
C11D 7/24
C11D 7/26
H01L 21/3065

(21)Application number : 11-361394

(22)Date of filing : 20.12.1999

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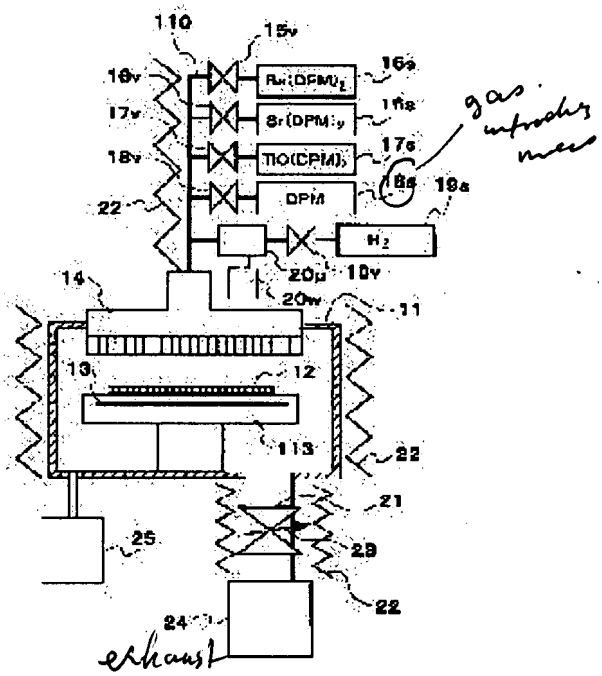
(54) DEVICE AND METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICE, AND CLEANING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a cleaning method for cleaning the inside of a device which films or etch a material containing alkaline-earth metal.

SOLUTION: A gas-introducing means 18s introduces gas which complexes alkaline-earth metal into a semiconductor manufacturing device 11. Consequently, the alkaline-earth metal in unuanted deposits in the device 11 are made into a complex, and produced gas is discharged from an exhausting device 24. As the gas for complexing, gas containing β diketone gas and cyclopentadiene gas is used.

図1



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[Date of request for examination]

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[Patent number]

[Date of registration]

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[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]